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US Army Research Laboratory

Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO)

by Edward FC Byrd

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14. ABSTRACT

The US Army Research Laboratory–developed series of scripts, written to dramatically simplify the computation of crystalline density and heat of formation, were used to evaluate the performance properties for the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (**1**) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (**2**) notional energetic materials. Additionally, a qualitative estimation of the impact sensitivities has been calculated. This report outlines the procedures used to generate this information, as well as Cheetah calculations using the predicted crystalline density and heat of formation.

15. SUBJECT TERMS

computational toolbox, script, crystalline density, heat of formation, impact sensitivity, energetic materials

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1. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation,[1,2] densities,[3,4] and impact sensitivity[5] of energetic materials, and have begun growing advanced synthesis capabilities to realize notional materials. This dual capability allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. For an in-depth explanation of the different theoretical methods employed herein, please refer to previous works.[6,7] This technical note will detail theoretical predictions of heat of formation, density, sensitivity, and performance for the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (**1**) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (**2**).[8]

2. Results and Discussion

The properties of **1** and **2** (Figs. 1a–b) were predicted using the ARL-developed scripts described in more detail in a previous report.[7] For the estimation of the impact sensitivities, the electrostatic maps on the 0.001 isosurfaces were generated with the scalar range of the electrostatic surface potential (ESP) ranging from –0.05 to 0.075. Recall that for this visualization methodology, regions of large positive charge (i.e., electron deficient regions, labeled as red) over the backbone of the structure tend to indicate increased sensitivity.

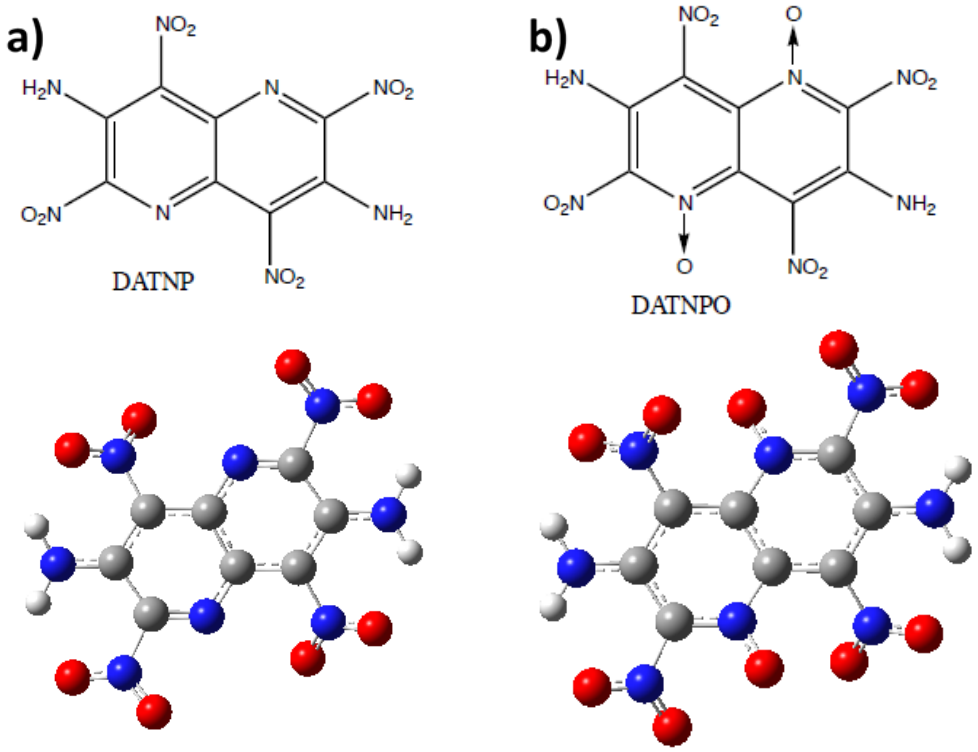

Fig. 1 Optimized structure of a) 1 and b) 2

The computed heats of formation and crystalline densities for these molecules are presented in Table 1.

Table 1 Computed heats of formation and crystalline densities for 1 and 2

Molecule	Solid phase heat of formation (kcal/mol)	Density (g/cm^3)
1	25.899	1.863
2	46.903	1.932

Additionally, we plot the ESP maps for **1** (Figs. 2a–b) and **2** (Figs. 3a–b) with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify both molecules as slightly sensitive to insensitive. We performed Cheetah 8.0 calculations[9] to predict the performance parameters using the predicted heats of formation and densities. At the Chapman-Jouguet point, Cheetah yields the values shown in Table 2.

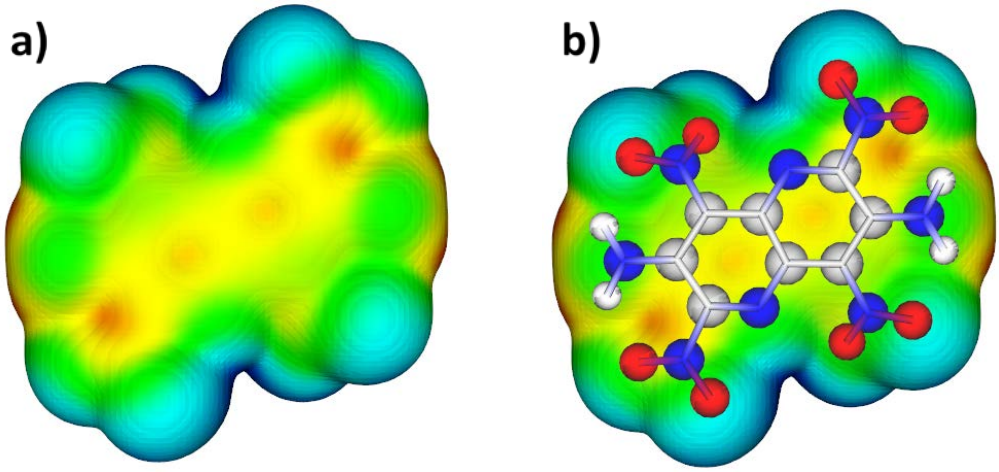

Fig. 2 Electrostatic potential map of 1, without a) and with b) molecule overlay

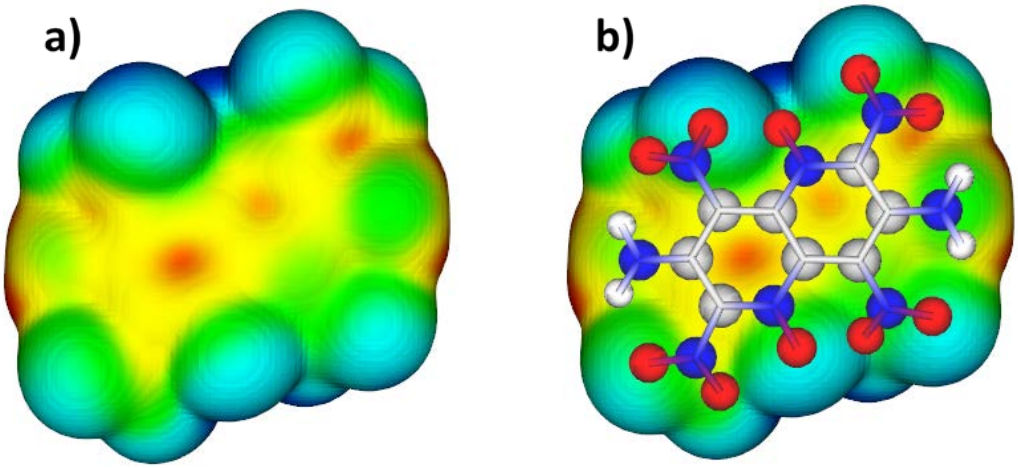

Fig. 3 Electrostatic potential map of 2, without a) and with b) molecule overlay

Table 2 Cheetah predicted properties for 1 and 2

Molecule	Pressure (GPa)	Shock velocity (km/s)	Temperature (K)	Total energy of detonation (TNT eqv. per cm^3)	Total energy of detonation (TNT eqv. per g)
1	27.182	8.033	3204.0	1.175	1.043
2	32.745	8.643	3692.8	1.397	1.196

Note: TNT = trinitrotoluene

3. Conclusions

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (**1**) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (**2**) molecules. Using this predicted data, we then ran Cheetah calculations to predict the performance of these materials. Additionally, we predicted the qualitative impact sensitivities of these compounds using electrostatic potential maps. This information has been transitioned back to the requesting synthetic chemist, Dr Gary K Windler of Los Alamos National Laboratory.

4. References

1. Byrd EFC, Rice BM. Improved prediction of heats of formation of energetic materials using quantum mechanical calculations. J Phys Chem A. 2006;110(3):1005–1013; ibid 2009;113:5813.

2. Byrd EFC, Rice BM. A comparison of methods to predict solid phase heats of formation of molecular energetic salts. J Phys Chem A. 2009;113(1):345–352.

3. Rice BM, Hare JJ, Byrd EFC. Accurate predictions of crystal densities using quantum mechanical molecular volumes. J Phys Chem A. 2007;111(42): 10874–10879.

4. Rice BM, Byrd EFC. Evaluation of electrostatic descriptors for predicting crystalline density. J Comp Chem. 2013;34(25):2146–2151.

5. Rice BM, Hare JJ. A quantum mechanical investigation of the relation between impact sensitivity and the charge distribution in energetic molecules. J Phys Chem A. 2002;106(9):1770–1783.

6. Byrd EFC. Theoretical prediction of the heat of formation, density and relative sensitivity for 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine. Aberdeen Proving Ground (MD): Army Research Laboratory (US): 2015 Apr. Report No.: ARL-TN-0680.

7. Byrd EFC. On the failure of correlating partitioned electrostatic surface potentials using Bader's atoms-in-molecules theory to impact sensitivities. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Sep. Report No.: ARL-TR-6206.

8. Windler GK. Los Alamos National Laboratory, Los Alamos, NM. Private communications, 2015 Sep.

9. Bastea S, Fried LE, Glaeseman KR, Howard WM, Kuo IFW, Souers PC, Vitello PA. Cheetah 8.0 thermochemical code. Livermore (CA): Energetic Materials Center, Lawrence Livermore National Laboratory; 2015.

List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
cm^3	grams per cubic centimeter
DATNP	3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene
DATNPO	3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide
DSRC	Department of Defense (DOD) Supercomputing Resource Center
ESP	electrostatic surface potential
kcal/mol	kilocalories per mole (unit of energy)
TNT	trinitrotoluene

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